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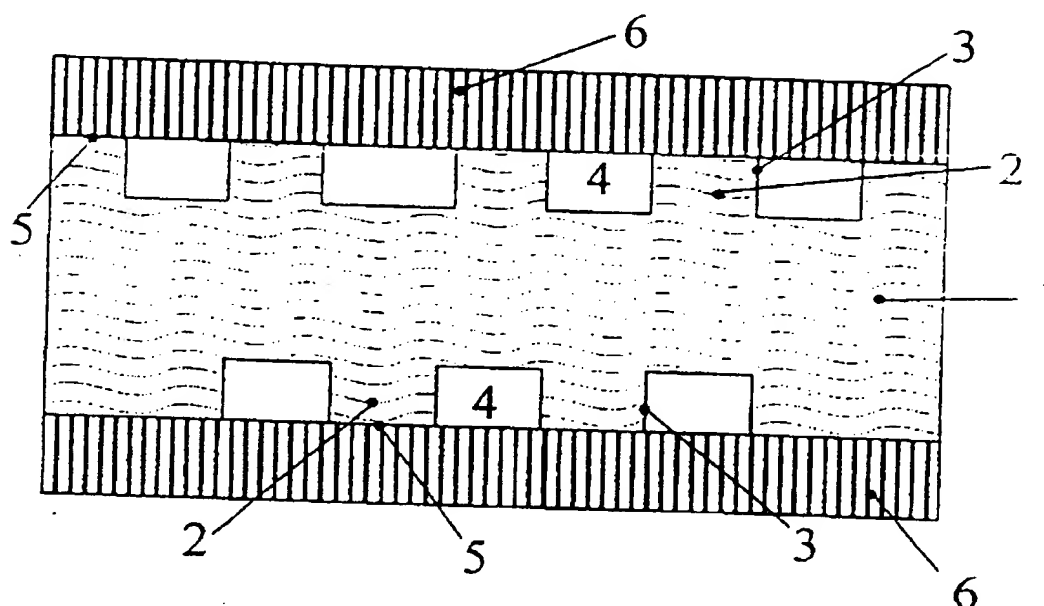
(12)(19)(CA) **Demande-Application**

(21)(A1) **2,240,270**

(86) 1996/12/06

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 (51) Int.Cl.<sup>6</sup> H01M 8/02  
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 (54) **PLAQUE BIPOLAIRE A PLACAGE SELECTIF**  
 (54) **SELECTIVELY COATED BIPOLAR PLATE**



(57) L'invention concerne une plaque bipolaire (1) qui est constituée d'un alliage formant de l'oxyde de chrome, qui présente une couche électroisolante réduisant les effets de la corrosion, située dans la zone des surfaces de guidage de gaz (3). Ladite plaque comporte une couche d'oxydes mixtes se trouvant sur la surface de contact d'électrode (5) et conçue pour augmenter la conductivité et réduire le taux d'évaporation. L'invention se rapporte également à un procédé de production de ladite plaque bipolaire, qui consiste à utiliser un alliage formant de l'oxyde de chrome en tant que matériau de base pour la plaque ainsi

(57) The invention relates to a bipolar plate (1) consisting of a chromium oxide-forming alloy with an electrically insulating, corrosion-reducing layer in the region of the gas guiding surfaces (3). Said layer has a mixed oxide layer on the electrode contact surface (5) to improve the conductivity and reduce the evaporation rate. The invention also relates to a process for producing the bipolar plate in which a chromium oxide-forming alloy is used as the plate material and an electrically insulating, corrosion-reducing surface coating is applied in the region of the gas guiding surfaces. The surface is then electrochemically coated with metals from which is

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qu'un revêtement de surface électroisolant, réduisant la corrosion dans la zone des surfaces de guidage de gaz. La surface est ensuite recouverte selon un procédé électrochimique avec des métaux à partir desquels se forme une couche d'oxyde présentant une conductivité élevée et un taux d'évaporation réduit par rapport à un alliage formant de l'oxyde de chrome, utilisé dans une pile à combustible. L'invention porte aussi sur une plaque constituée d'un alliage formant de l'oxyde de chrome, et présentant des couches d'enrichissement, au cobalt, nickel ou fer, dans la zone de la surface de contact d'électrode.

formed an oxide layer of high conductivity and low evaporation rate in comparison with the chromium oxide-forming alloy when used in the fuel cell. The invention also relates to a plate consisting of a chromium oxide-forming alloy with cobalt, nickel or iron enrichment layers in the region of the electrode contact surface.



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**(57) Abstract**

The invention relates to a bipolar plate (1) consisting of a chromium oxide-forming alloy with an electrically insulating, corrosion-reducing layer in the region of the gas guiding surfaces (3). Said layer has a mixed oxide layer on the electrode contact surface (5) to improve the conductivity and reduce the evaporation rate. The invention also relates to a process for producing the bipolar plate in which a chromium oxide-forming alloy is used as the plate material and an electrically insulating, corrosion-reducing surface coating is applied in the region of the gas guiding surfaces. The surface is then electrochemically coated with metals from which is formed an oxide layer of high conductivity and low evaporation rate in comparison with the chromium oxide-forming alloy when used in the fuel cell. The invention also relates to a plate consisting of a chromium oxide-forming alloy with cobalt, nickel or iron enrichment layers in the region of the electrode contact surface.

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## Selectively Coated Bipolar Plate

The present invention relates to a bipolar plate for a high-temperature fuel cell, said plate consisting of a chromium oxide-forming alloy with a corrosion-reducing layer in the region of the gas guiding surfaces, and a process for producing this plate. A bipolar plate of this kind and a process for producing it are described in DE 44 10 711 C1.

A high temperature fuel cell (solid oxide fuel cell - SOFC) permits the direct conversion of chemical energy into electrical energy. The fuel ( $H_2$ ,  $CH_4$ ,  $CO$ , etc.) is separated from an oxidizing agent ( $O_2$ , air,) by a solid electrolyte (Y-stabilised  $ZrO_2$ ) that conducts oxygen. At a cell-operating temperature of approximately  $950^\circ C$ , oxygen ions are conducted from the cathode side through the electrolytes that react with the fuel at the anode. Because of charge equalisation, a stream of electrons flows in the same direction.

In order that these reactions can proceed at sufficiently high levels of conversion, the electrolyte must be coated with porous electrolyte materials that act catalytically. Generally speaking, the anode (fuel side) consists of an  $Ni/ZrO_2$ -cermet and the cathode (oxygen side) is of  $LaMn$  perovskite.

The voltage that can be tapped off from a single cell is extremely low (less than 1 V). Because of this, several cells have to be connected together; thus, an additional cell component, namely the bipolar plate (also referred to as the interconnector) is needed in order to be able to use

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SOFC technology for generating current. In contrast to the electrolytes and the electrodes, which are in the order of 100  $\mu\text{m}$  thick, in the SOFC flat cell concept that is discussed today, the bipolar plate is several millimetres thick and thus forms not only the gas-conducting connecting element between the individual cells, but also the supporting component for the cell (EP 0338 823 A1).

At operating temperatures of up to the order of 1000°C, the bipolar plate must possess the following properties: sufficient mechanical strength, impermeability to gas, simple (cost effective) production, thermal expansion that is close to that of the ceramic material used for the electrodes, good electrical conductivity, resistance to corrosion in the oxidizing gas (air) and with the fuel ( $\text{H}_2\text{O}/\text{H}_2$ ), and compatibility with the materials used for the electrodes. It must also be simple and economical to manufacture.

At the present time, two groups of materials are considered for bipolar plates: ceramics based on  $\text{LaCrO}_3$  and metallic high-temperature materials. Recently, because of their greater strength, better electrical conductivity, and the fact that they are simpler to machine, the latter are being favoured. Because of the resistance to hot-gas corrosion that is required, only high temperature materials that form  $\text{Cr}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  are considered. In this regard, generally speaking alloys that are based on NiCr or FeNiCr are not considered because their coefficients of thermal expansion are too high ( $\approx 20 \cdot 10^{-6} \text{ K}^{-1}$  compared to  $10 \cdot 10^{-6} \text{ K}^{-1}$  for electrolyte/electrodes) in the light of today's knowledge.

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In general, it can be stated that alloys that form  $\text{Al}_2\text{O}_3$  with a very low layer growth exhibit better resistance to corrosion than alloys that form  $\text{Cr}_2\text{O}_3$ . However, because of the formation of the  $\text{Al}_2\text{O}_3$ , problems occur because of increased transitional resistance at the contact points between the bipolar plate and the electrodes. For this reason, alloys that form chromium oxide are used as material for the interconnector, with the alloys that are based on Cr or Fe Cr being preferred above the others. These entail the additional advantage that their coefficients of thermal expansion are very small. However, the thicker oxide layers, which form relatively rapidly, are not mechanically stable. They chip off and can thus restrict the flow of gas into the gas channels over a longer period of operation. In addition, the thick layers of  $\text{Cr}_2\text{O}_3$  that form after longer periods display low electrical conductivity, and at high oxygen pressures (such as those on the cathode side) they form volatile chromium oxides or hydroxides that contaminate the cathode or the cathode/electrolyte boundary surface.

In order to solve the problem of the mechanically unstable oxide layers that form, DE 44 10 711 C1 proposes using an alloy that forms chromium oxide as the material for the bipolar plate. In the region of the gas-conducting surfaces, the alloy is provided with a protective layer of aluminum. At the high temperatures that prevail within the fuel cell, the surface of the aluminum layer is converted to a layer of  $\text{Al}_2\text{O}_3$ . The  $\text{Al}_2\text{O}_3$  reduces the corrosion effects.

However, in the case of this bipolar plate, the disadvantageous effects of the chromium oxide layers that form in the region of the contact surfaces between the electrodes and the bipolar plate have to be accepted as they are.

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It is known from DE 42 42 570 A1 that in addition to the alloys that are based on FeCr and Cr, a mixture of CrNi alloy and 50 to 85% by weight (relative to the mixture) of oxide ceramic can be used as the material for the connectors, said oxide ceramic consisting in particular of silicon oxide or aluminum oxide; this also serves to adjust the coefficients of thermal expansion. However, the document makes no mention of any special details of the embodiment or its potential behaviour as a bipolar plate.

Even in the case of this bipolar plate, it is to be expected that chromium oxide layers with the above discussed problems will occur.

It is the task of the present invention to create a bipolar plate that, in addition to being simple to manufacture, is resistant to oxidation, exhibits good conductivity at the boundary surface with the electrodes, and exhibits a low evaporation rate with respect to volatile chromium oxide/hydroxides.

This problem has been solved by a bipolar plate with the features set out in the apparatus claims. Advantageous configurations are set out in the secondary claims relating thereto. This problem has also been solved by a process having the features set out in the process claim.

The electrode contact surface is the boundary surface between the bipolar plate and the electrodes.

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A mixed-oxide layer to enhance conductivity and reduce the rate of evaporation can be achieved, for example, by applying a thin layer of a metal or metallic oxides that form a mixed oxide (e.g., of the Spinell type) on the oxide/gas boundary surface when used at the high temperatures with Cr and/or  $\text{Cr}_2\text{O}_3$ . This mixed oxide must exhibit a lower rate of evaporation than  $\text{Cr}_2\text{O}_3$  and, in addition, must increase the electrical conductivity of the  $\text{Cr}_2\text{O}_3$  by incorporating metal ions into it.

Metals or their oxides that are suitable for this purpose are, for example, Ni, Co, or Fe, with nickel having the greatest effect on the electrical conductivity of  $\text{Cr}_2\text{O}_3$ .

The metals or their oxides can be applied, for example, by the usual PVD or CVD process. In addition, a cost-effective process for metals is galvanic deposition or electroplating.

According to the main claim and the related secondary claims, a corrosion-reducing, electrically insulating layer is provided in the region of the gas guiding surfaces. The fact that this layer is electrically insulating permits--in a very simple manner--selective production of different protective layers on the bipolar plate, these layers possessing optimal properties with reference to the demands that are made. For example, in the region of the gas guiding surfaces, it is possible to provide an  $\text{Al}_2\text{O}_3$  protective layer that displays excellent corrosion-reducing properties. In addition, the fact that this layer is also electrically insulating makes it possible to apply a different protective layer in the region of the electrode contact surfaces and, most advantageously, to do this by using a simple, electrochemical process. Thus, it is



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possible to apply an additional protective layer with other physical properties, namely electrically conductive properties, in the region of the electrode contact surfaces.

Using the present process in order to manufacture a bipolar plate, a suitable chromium oxide forming alloy as described in DE 44 10 711 C1 is coated in such a way that a surface coating

5 is effected in the region of the gas conducting surfaces, this coating being an electrical insulator and reducing corrosion.

Such coating can be effected, for example, in the form of an  $\text{Al}_2\text{O}_3$  surface coating in the region of the gas guiding surfaces.

10

To this end, for example, the surface of the bipolar plate is enriched with aluminum. The enrichment layer is pre-oxidized at temperatures of, for example,  $1000^\circ\text{C}$  so that  $\text{Al}_2\text{O}_3$  forms over the whole surface of the interconnector. The oxide layer and the zone enriched with aluminum are removed from the surfaces of the ribs of the bipolar plate (i.e., from the surfaces

15 that are in contact with the electrodes) by means of a conventional grinding process.

The thickness of the layer should amount to a few  $\mu\text{m}$ . It is especially preferred that the layer be from 1 to 3  $\mu\text{m}$  thick.

20 Next, the surface is electrochemically coated with metals that form an oxide layer of increased conductivity and a reduced evaporation rate as compared to be alloys that form chromium oxide when used in the fuel cell. Coating is effected using an electrochemical process in order that no more coating takes place in the region of the gas guiding surfaces. This is done, for

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example, by galvanic coating. Suitable metals are, for example, Ni, Co, or Fe. The result is layered enrichment in the sense of the subordinate apparatus claim.

It is preferred that a thin layer of, for example, approximately 1 - 10  $\mu\text{m}$ , and in particular 1 - 3  $\mu\text{m}$  be deposited electrochemically. Because of the fact that there is a layer with electrically insulating properties present on the walls of the gas channels, no metallic deposition takes place at these points. Deposition is effected only on those parts of the bipolar plate that are metallicity bare, in other words, on the surfaces of the ribs (electrode contact surface is), as desired.

Using this process, a selectively coated bipolar plate is produced, this consisting of an alloy that forms chromium oxide. In the region of the gas guiding surfaces, this plate has a protective layer that reduces corrosion effects and which is an electrical insulator. As an example, this can be a thin layer of  $\text{Al}_2\text{O}_3$ . For the remainder, it is covered with a metallic coating on the electrode contact surfaces. Iron, nickel, or cobalt are considered since these modify the physical properties of the  $\text{Cr}_2\text{O}_3$ , as is desired.

Chromium, NiCr, FeCr, and chromium-nickel alloys are suitable as materials for bipolar plates.

However, it is preferred that chromium or iron-chromium alloys be used. An enrichment layer on the walls of the gas channels, consisting of aluminum, should be between 20 and 200  $\mu\text{m}$  thick, and in particular 50 to 100  $\mu\text{m}$  thick. The metallic layer on the surfaces of the ribs should be from 1-10  $\mu\text{m}$  and in particular 1-3  $\mu\text{m}$  thick.

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The present invention will be described in greater detail below on the basis of the drawings appended hereto. These drawings show following:

Figure 1: a cross section through a bipolar plate arranged between anode and cathode;

Figure 2: a section of a bipolar plate and the individual steps involved in selective coating.

Figure 1 shows the bipolar plate 1 that is of a chromium oxide-forming alloy for temperatures  $\geq 900^{\circ}\text{C}$  and of a ferritic steel with 12 - 35%-wt chromium for temperatures  $\leq 900^{\circ}\text{C}$ . The typical shape (a plate that is a few millimetres thick, with gas channels) can be manufactured from sheet metal using metal-cutting processes, or by means of a near-net-shape process using a powder-metal method (MIM, WPP). The ribs 2 on the plate 1, which form the side walls 3 of the gas channels 4, are first machined so as to be slightly higher than is desired in the end form (Figure 2a), in order to take into account the subsequent removal of Al-enrichment layers 7 and oxide layers 8 on the contact surfaces 5 between the bipolar plate 1 and the electrodes 6 (face surfaces).

The bipolar plate produced in this way is subjected to a conventional alitizing process. To this end, the plate is aged in a powder mixture made up of an inert material (e.g.,  $\text{Al}_2\text{O}_3$ , 90%), a chloride/fluoride activator (e.g.,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ , 5%, and Al powder (5%) at an elevated temperature (600 -  $1300^{\circ}\text{C}$ ) in a protective-gas atmosphere (e.g., argon). Typical alitizing conditions would be 3 hours at  $1000^{\circ}\text{C}$ . This produces an Al-enriched zone 7, as in Figure 2a, on the surface of the plate (face surface 5 of the ribs and walls 3 of the gas channels). If an alloy based on chromium is present, then, for example, intermetallic phases of the  $\text{Cr}_3\text{Al}_8$  or

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Cr<sub>4</sub>Al<sub>3</sub> type will be formed. Different alitizing techniques or other methods can be used to enrich the surface with aluminum should this be desirable for reasons of process technology, e.g., in the case of CVD, PVD, or mechanical coating.

- 5 After aluminum enrichment, the pre-oxidation shown in Figure 2b is effected in order to former a thin Al<sub>2</sub>O<sub>3</sub> layer 8 on the surface of the interconnector (e.g., by oxidation in air at 1000°C for 1 hour).

10 The Al<sub>2</sub>O<sub>3</sub> layer and the aluminum-enriched layer 7 are removed from the face surface 5 of the ribs 2 by simple area machining (e.g., grinding). The original over-size dimensions of these areas takes the thickness of the material to be removed by grinding into account. The over-size dimensions must be greater than the thickness of the Al<sub>2</sub>O<sub>3</sub> layer 8 plus the depth to which the the aluminum penetrates into the aluminum-enriched zone 7 (See Figure 2c).

- 15 This is followed by coating (coating thickness 1 - 10 and in particular 1 to 3 μm) with Ni, Fe, or Co, using an electrochemical process (e.g. galvanic deposition). Because of the Al<sub>2</sub>O<sub>3</sub> layer that is present on the gas channels walls, no metals is deposited in these places. As desired, deposition takes place only on the surface of the ribs 5, i.e., at the boundary surfaces between the interconnector and the electrodes (Figure 2d). This means that, in its final form, the
- 20 bipolar plate has a thin layer 9 of metal (nickel, iron, cobalt) on the base material (e.g., alloys based on chromium or ferritic FeCr alloy) on the face surfaces 5 of the ribs 2, whereas on the "walls" of the gas channels there is an aluminum-rich layer 7 that is covered with a thin Al<sub>2</sub>O<sub>3</sub> layer 8.

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Under operating conditions ( approximately 950°C in air/O<sub>2</sub> or in H<sub>2</sub>/H<sub>2</sub>O , or in other fuel mixtures, the bipolar plate produced in this way forms the desired layer that is based on Cr<sub>2</sub>O<sub>3</sub> on the surface 5 of the ribs 2 (i.e., at the contact points with the electrodes); this layer is enriched with Fe, Ni, or Co and is covered at the boundary surfaces with the gas with a mixed oxide (e.g., CrNi, Cr/Co or Cr/Fe-Spinell), whereas Al<sub>2</sub>O<sub>3</sub> continues to grow on the walls of the gas channels.

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## Patent Claims

1. A bipolar plate (1) that is of a chromium oxide-forming alloy with an electrically-insulating, corrosion-reducing layer in the region of the gas guiding surfaces (3), characterised by a mixed oxide layer that is located on the electrode contact surfaces (5) to increase conductivity and to reduce the rate of evaporation.
2. A bipolar plate as defined in one of the preceding Claims, in which the metal oxide layer that is located on the electrode contact surfaces (5) contains nickel, cobalt, or iron.
3. A bipolar plate as defined in one of the preceding Claims, in which the mixed oxide layer that is located on the electrode contact surface 5 is less than 3  $\mu\text{m}$  thick.
4. A bipolar plate as defined in one of the preceding Claims, in which the layer that reduces the corrosion effects in the region of the gas-guiding surfaces (3) is enriched with aluminum.
5. A bipolar plate consisting of an alloy that forms chromium oxide which has on the electrode contact surface (5) layered enrichment with nickel, cobalt, or iron.
6. A process for manufacturing a bipolar plate in which a chromium oxide-forming alloy is used as the plate material, and in which coating with an electrically insulating and corrosion reducing surface layer is effected in the region of the gas-guiding surfaces,

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characterised by subsequent electrochemical coating of the surface, particularly of the electrode contact surface (5), with metal from which an oxide layer with a high level of conductivity and a low evaporation rate as compared to chromium oxide forming alloys is formed when used in the fuel cell.

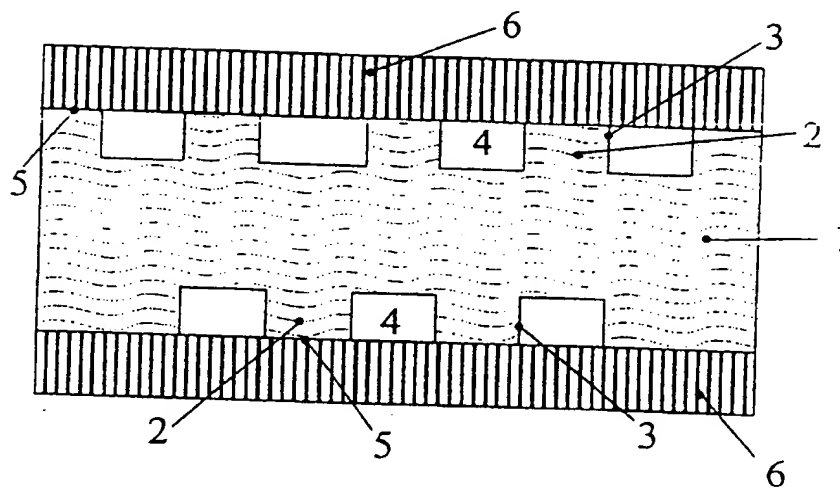
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Figur 1

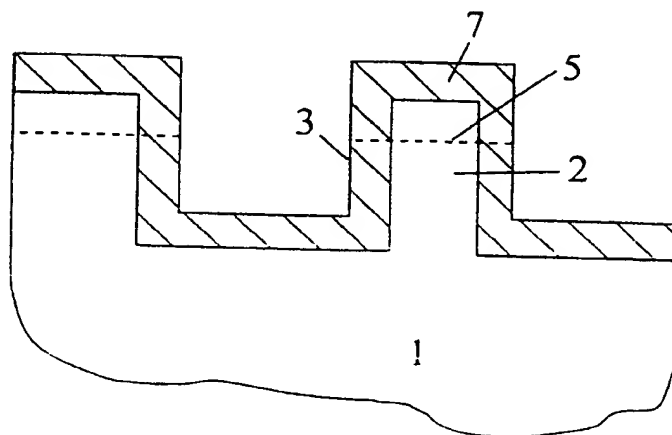
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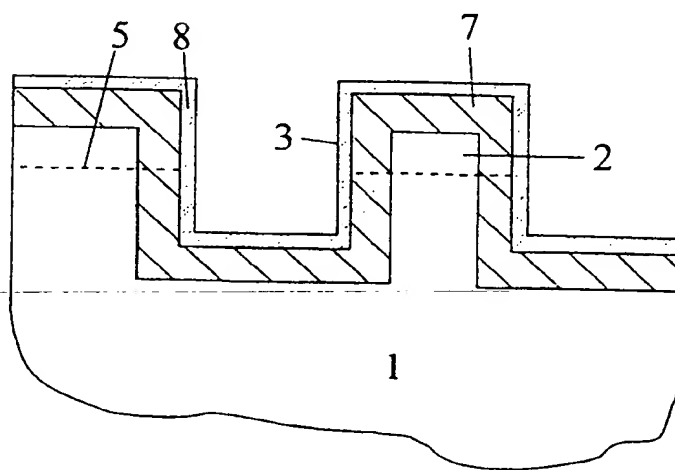
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Figur 2a



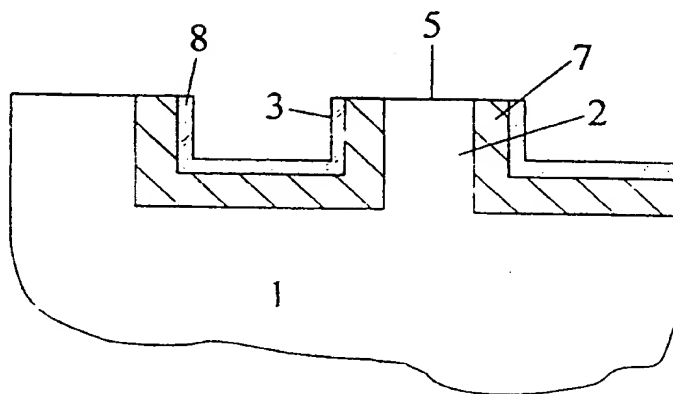
Figur 2b

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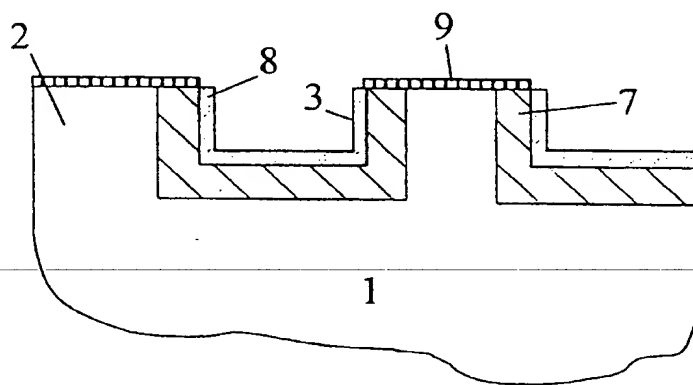
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Figur 2c



Figur 2d

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